



Application Note  
CBRNE #705406

## Rapid On-Site Detection of PAHs and PCBs in Soil Samples Using the Mobile E<sup>2</sup>M Detection System

### Abstract

E<sup>2</sup>M equipped with an air/surface probe is designed for on-site identification of hazardous substances in different media (soil, water, air) by determining the target mass spectra. This is achieved within minutes and without the need for sample preparation.

The air/surface probe, that contains a short, heated GC column, was used in combination with the E<sup>2</sup>M for identification of Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) in complex soil samples.

### Introduction

Organic pollutants like Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) are widespread toxic and Persistent Organic Pollutants (POPs).

PAHs consist of fused aromatic rings without heteroatoms or substituents. The simplest example for this class of compounds is naphthalene (Figure 1a). PAHs are formed by an incomplete combustion of organic material like fuel, coal or tobacco and are present in oil, coal and in large amounts in tar deposits. In the environment PAHs are found

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Polycyclic aromatic hydrocarbons (PAH)	Monitoring List Editor
Polychlorinated biphenyls (PCB)	E <sup>2</sup> M Control
	DataAnalysis

in high concentrations near highways and in places where tar has been used (such as road construction, wooden railway sleepers or telegraph poles) or tar was formed (gas stations, coking plants) [1, 2].

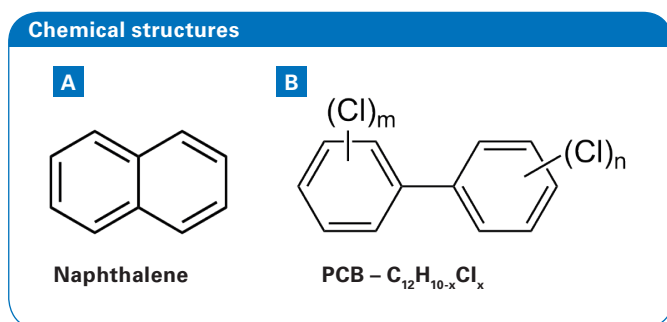


Figure 1: Chemical structure of the PAH naphthalene and of chlorinated biphenyl.

A PCB is any of the 209 different configurations of chlorinated biphenyl with 1 to 10 chlorine atoms (Figure 1b). PCBs were used as coolant fluids in transformers, capacitors and electric motors, as plasticizers in paints and cements and in sealants for caulking. Their chronic toxicity is evident even at low amounts [3, 4] (Tolerable Daily Intake (TDI) for mixtures of PCB: 0.02 µg/kg/day [5]). PCBs are accumulated in adipose tissues of organisms at the end of the food chain [6, 7]. PCBs are among the “dirty dozen” POPs that were banned by the Stockholm Convention on Persistent Organic Pollutants, a legally binding international agreement that was signed by more than 100 countries in May 2001.

Most of the available field testing methods for PCBs are designed to test the PCB content in oil or water. PCB tests for soil or solids are rare and only specific for organic chlorides [7] and not for identification of PCBs themselves. Conventionally, these hazardous substances are tested by taking samples on-site and then analyzing them in a laboratory.

In this application note we describe a fast on site detection method. This method requires no additional sample preparation or laboratory and results are available in minutes.

## Experimental

### Material

The following certified soil standards were purchased from the Federal Institute for Materials Research and Testing (BAM) in Germany:

- ERM-CC013a certified values for PAH (between 1 and 12.9 mg/kg depending on the compound)
- BAM-U019 certified values for PCB (between 0.5 and 2.96 mg/kg depending on the compound)

Synthetic standards to determine the mass spectra of the single compounds were purchased from NEOCHEMA, Germany:

- 14022 PAK Mix 16 (each 100 µg/ml)
- 15002 PCB Mix 6 (each 100 µg/ml)

### Instrumentation

The analyses were performed on an E<sup>2</sup>M mass spectrometer equipped with an air/surface probe. The probe head and the probe line of the air/surface probe are heated separately to 240 °C. This enables monitoring of substances at a constant temperature or performing a temperature run. The probe line consists of a MXT 5 GC capillary (l 3.5 m, ID 0.53 mm, 0.25 µm film), a heater and insulation.

### Analytical conditions

Temperature run (programmed temperature gradient for running the air/surface probe similar to a GC):  
 Probe head 220°C, start temperature probe line: 90°C hold for 30 seconds, temperature gradient probe line: 20°C/min to 220°C hold for 1000 seconds, inlet valve 220°C.

Monitoring method (detection of defined compounds):  
 Probe head 220°C, probe line 200°C, inlet valve 200°C (Compound parameter see Table 1).

### Detection of PAHs and PCBs

PAH and PCB standards, respectively, were diluted in methanol and placed in an aluminum cup. The air/surface probe was pressed directly onto the samples for 60 seconds. Complex soil samples were analyzed by placing 1 g of ERM-CC013a or BAM-U019 into an aluminum cup, adding 250 µl of methanol and pressing the probe onto the sample for 60 seconds (Figure 2).

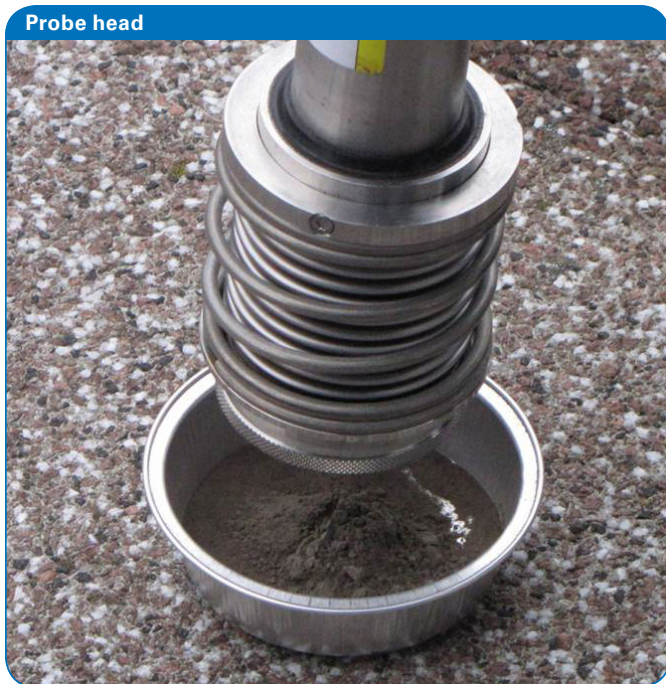


Figure 2: Pressing the probe head directly onto the contaminated soil sample.

## Results

Generation of a monitoring method for detection of PCB and PAH

The monitoring method is a “Selected Ion Monitoring” (SIM) method enabling the detection of specific compounds with an enhanced sensitivity relative to the full scan mode. Measured ions - typically two to four - are compared to the masses defined in a monitoring list. In this list parameters like alarm and warning limits as well as interference and reliability for each compound are defined. An alarm is triggered when the concentration of the compound is high enough to exceed the defined alarm threshold and the masses ( $m/z$ ) and relative intensity of the single masses are within the limits defined by parameters as interference and reliability. In the monitoring window the alarm is shown by red bars. Yellow bars indicate that the warning limit is exceeded but the concentration is not high enough to trigger an alarm. Green bars indicate that some of the masses match but not all of them, or that they are not in the right ratio defined in the monitoring list.

To create a monitoring method the masses ( $m/z$ ) and the relative intensities are required. This information can either be obtained from the NIST library or by mass spectra acquired with the E<sup>2</sup>M. Table 1 summarizes the monitoring list parameters and available boiling points for PAHs and PCBs. Because a differentiation of the PCB by congener is not possible, they are named by the number of Cl- atoms.

Table 1: Monitoring list parameters and boiling points of PAHs and PCBs.

Monitoring list parameters								
Compound(s)	Compound name	Abbreviation	Boiling point [°C]	Masses (m/z)	Relative Intensities [%]			
Naphthalene	PAH C10	NAP	218	<b>128</b>	<b>100</b>			
				129	11			
				127	11			
Acenaphthene	PAH C12	ACE	279	<b>153</b>	<b>100</b>			
				154	83			
				152	51			
Acenaphthylene	C12	ACY	280	151	19			
				<b>166</b>	<b>100</b>			
				165	84			
Fluorene	PAH C13	FLU	295	167	14			
				163	12			
				<b>178</b>	<b>100</b>			
Anthracene	PAH C14	ANC	340	179	22			
				Phenanthrene	PHT	332	176	17
							177	10
Fluoranthene	PAH C16	FLT	375	<b>202</b>	<b>100</b>			
				Pyrene	PYR	404	203	17
							200	15
Chrysene	PAH C18	CHR	448	201	12			
				Benz(a)anthracene	BAA	438	<b>228</b>	<b>100</b>
							226	27
Benz(a)pyrene	PAH C20	BAP	495	229	20			
				Benzo(b)fluoranthene	BBF	n.a.	227	11
							Benzo(k)fluoranthene	BKF
253	22							
Benzo(ghi)perylene	PAH C22	BPE	500	250	17			
				Indeno(1,2,3-cd)pyrene	INP	n.a.	126	12
							<b>276</b>	<b>100</b>
Dibenz(ah)anthracene	PAH C22a	DBA	n.a.	277	23			
				PCB 3Cl	PCB 3Cl	n.a.	274	20
							138	19
PCB 3Cl	PCB 3Cl	PCB 3Cl	n.a.	<b>278</b>	<b>100</b>			
				279	24			
				276	17			
PCB 4Cl	PCB 4Cl	PCB 4Cl	n.a.	139	12			
				<b>256</b>	<b>100</b>			
				258	96			
PCB 4Cl	PCB 4Cl	PCB 4Cl	n.a.	260	33			
				186	95			
				<b>292</b>	<b>100</b>			
PCB 4Cl	PCB 4Cl	PCB 4Cl	n.a.	290	74			
				294	42			
				220	38			
PCB 5Cl	PCB 5Cl	PCB 5Cl	n.a.	<b>326</b>	<b>100</b>			
				324	63			
				328	51			
PCB 5Cl	PCB 5Cl	PCB 5Cl	n.a.	254	39			
				<b>360</b>	<b>100</b>			
				362	81			
PCB 6Cl	PCB 6Cl	PCB 6Cl	n.a.	290	50			
				358	49			
				<b>394</b>	<b>100</b>			
PCB 6Cl	PCB 6Cl	PCB 6Cl	n.a.	396	98			
				398	54			
				392	44			
PCB 7Cl	PCB 7Cl	PCB 7Cl	n.a.					

A temperature run was performed using synthetic standards "PAK Mix 16" and "PCB Mix 6" in order to obtain the masses (m/z) with their relative intensities of the single compound groups. These values were added to the monitoring list. To avoid false alarms the most unique mass number combination for each compound was selected. An example for the assignment of the measured values is shown in figure 3.

In the chromatogram the "compound" ANC/PHT was selected. The mass numbers (m/z) and the relative intensities were picked from mass spectrum data (Figure 3) and inserted in the monitoring list. A monitoring method can consist of up to 20 compounds with 8 masses per compound. But in most of the cases 3 to 4 masses are enough to characterize a compound.

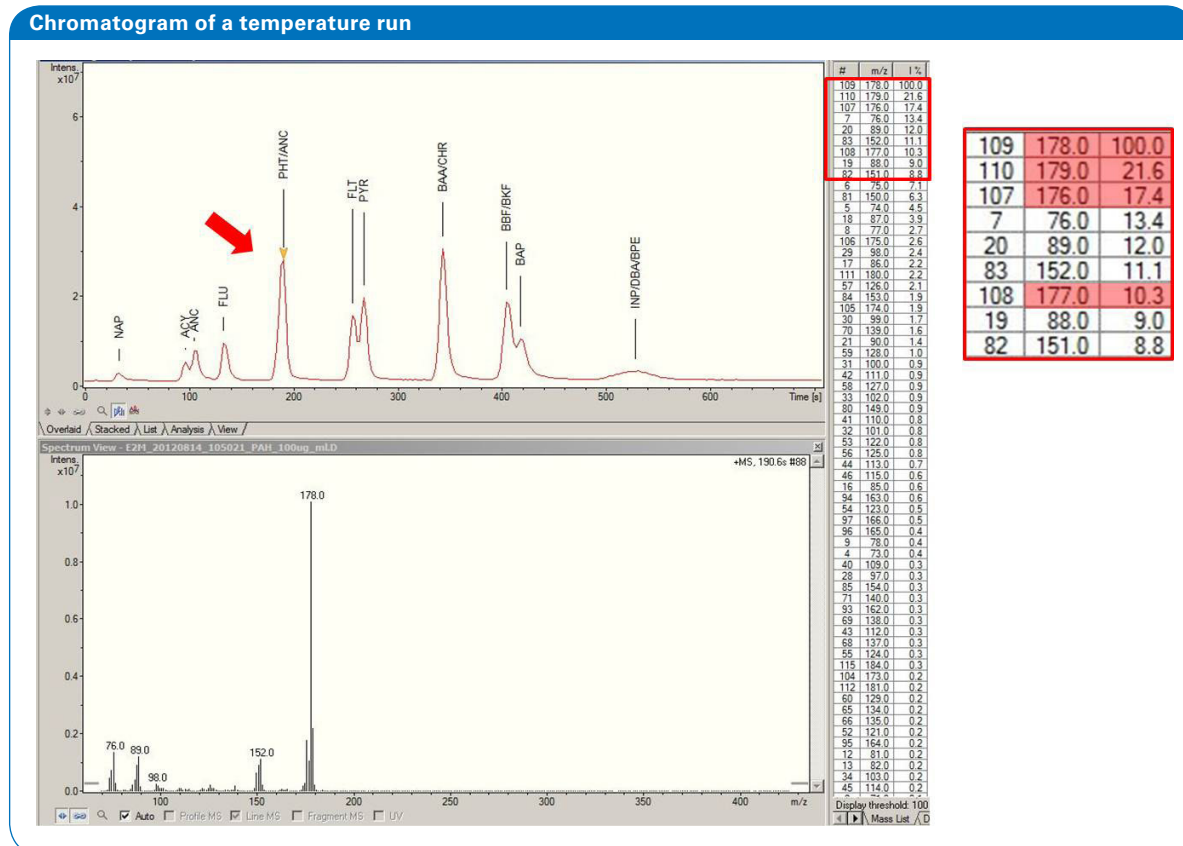


Figure 3: Chromatogram of a temperature run (synthetic standard "PAK Mix 16") with details of the data analysis software to demonstrate the creating of compounds in the monitoring list. Mass numbers and relative intensities inserted in the monitoring list are highlighted in red.

### Detection PAH and PCB in soil samples

The created monitoring method was used to detect PAH and PCB in soil samples. Using the PAH contaminated soil ERM-CC013a, some seconds after pressing the probe head on the samples an alarm for naphthalene (NAP) and fluorene (FLU) was triggered. The alarm for ANC/PHT and FLT/PYR followed after 30 seconds. The higher boiling compounds such as CHR/BAA require 60 seconds to pass the probe line. The group BAP/BBF/BKF when in soil, is not easy to mobilize and was therefore not detected. However, using the synthetic standard "PAK Mix 16" in a concentration of 0.5 µg of each compound an alarm for BAP/BBF/BKF was triggered within 3 minutes.

The detection of this high boiling PAH in the synthetic standard was achieved because the concentration was higher than in the soil sample and thus the mobilization of dissolved compounds is easier. Detecting the absent PAH (BPE, INP and DBA) despite this concentration range, is still not possible as these compounds are not mobile enough for detection using this method.

Pressing the probe onto the PCB contaminated soil BAM-U019 generated an alarm for PCB 3Cl and PCB 4Cl after 20 seconds, 9 seconds later the alarm for PCB 5Cl was triggered (Figure 4).

## Conclusion

Additionally, figure 4 represents an alarm for ANC/PHT and FLT/PYR. This is feasible because these PAHs are easy to mobilize and in soil samples they are often the highest concentrated PAHs. The presence of these PAHs was proved using a temperature run (Figure 5) and subsequent analyses of their mass spectra.

The E<sup>2</sup>M combined with the air/surface probe is a powerful solution for the detection of organic pollutions such as PCB and PAH. It is very fast, selective and requires little effort. No sample preparation is needed and sampling is simply achieved by pressing a heated air/surface probe head directly onto the target sample.

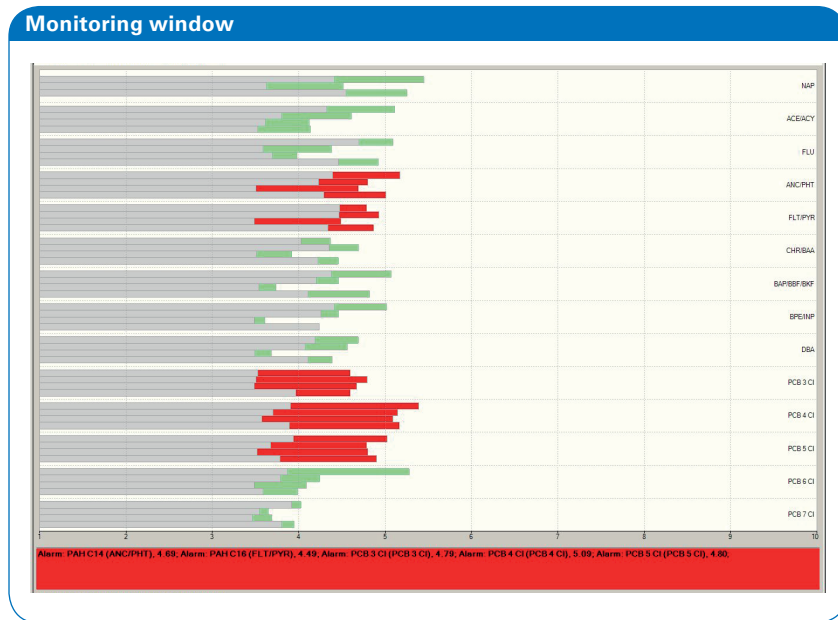


Figure 4: Detection of the PCB contaminated soil. An alarm (indicated by red bars) for PCB 3Cl, PCB 4Cl and PCB 5Cl and also for the PAH ANC/PHT and FLT/PYR was triggered (green bars indicate that some masses are measured but not all or not all in the ratio defined in the monitoring list).

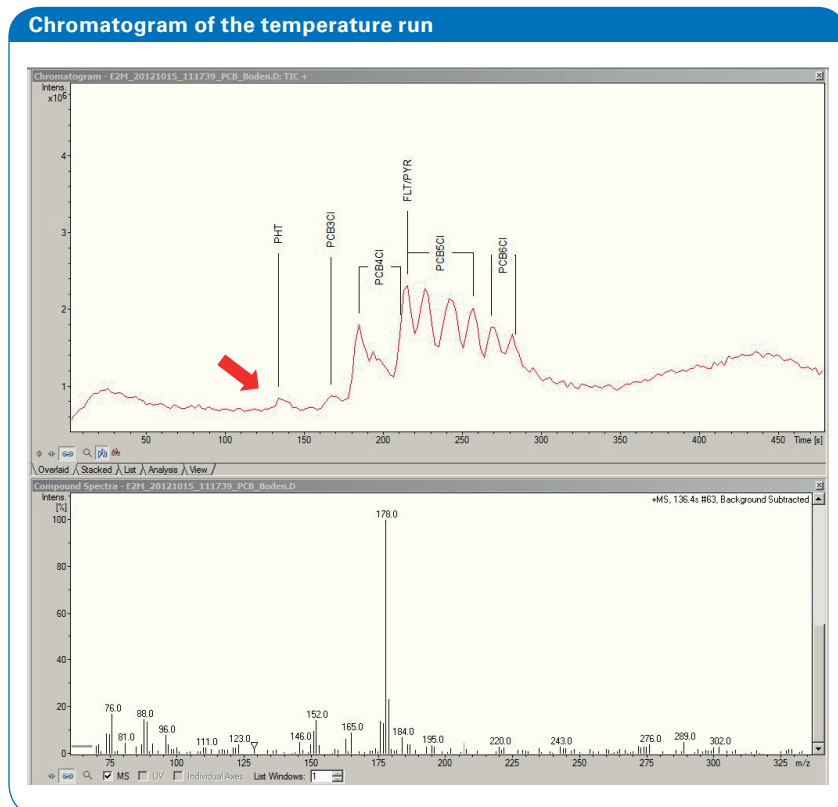


Figure 5: Chromatogram of the temperature run of the PCB contaminated soil BAM-U019, with the mass spectrum of the signal at 136 seconds that proves the presence of ANC/PHT.

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